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Towards the use of CO2 and the oxidizing potential of flue gases without prior separation to produce cyclic carbonates by a tandem catalytic process

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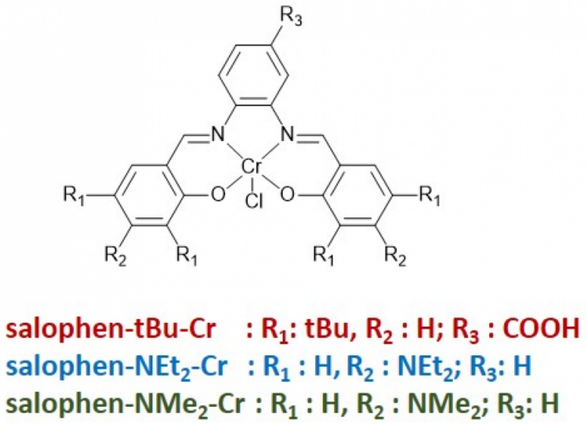
PURPOSE OF THE ABSTRACT

Many processes for the biological recovery of CO2 directly use industrial flue gases. In contrast, the chemical recovery of CO2 often requires that it is first separated from other components such as oxygen, nitrogen, water and other impurities. The most commonly used method is based on the absorption of CO2 by aqueous solutions of amines such as monoethanolamine, but the latter tends to be degraded due to the presence of oxygen [1]. In our group, we are aiming to take advantage of the oxidizing potential of O2 mixed with CO2 to produce cyclic carbonates, not from CO2 and epoxides but from O2, CO2 and alkenes in a one-pot process. Underlying this work is the requirement that the conditions for carrying out the aerobic epoxidation in the presence of aldehydes used as sacrificial electron donors (from room temperature to 80°C) are compatible with those of the cycloaddition of CO2 onto epoxides (often above 100°C and under about 10 bar of CO2). Indeed, previously, in our hands, the combination of the Jacobsen's complex (MnSalen) with isobutyraldehyde (IBA) for the aerobic epoxidation with an activated quaternary ammonium salt (C16H33N(Me)2(C2H4-OH)+Cl-) for CO2 cycloaddition under 5 bar of O2 and 15 bar of CO2 at 120°C was shown to be unsuccessful [2]. While we had established that epoxidation of styrene (St) at 80°C and cycloaddition to styrene oxide (SO) at 120°C were both successful, no styrene carbonate was produced by combining the two at 80°C (too low temperature for cycloaddition) or 120°C due to multiple side reactions resulting from the high temperature autoxidation of the excess aldehyde used [3].

In the present contribution, the conditions for the implementation of the CO2 cycloaddition onto styrene oxide have been revisited with the aim of enabling them to be compatible with aerobic epoxidation at 80°C. Thus, complexes of Ni(II), Mn(III) and Cr(III) with easy-to-synthesize ligands, such as H2Salophen-t-Bu (for N,N'-bis(3,5-di-tert-butysalicylidene)-1-carboxy-3,4-phenylenediamine) were prepared in yields between 50% (Mn(III)) and 90% (Cr(III)). The Lewis acid properties of these complexes were exploited in order to activate styrene oxide towards its nucleophilic attack by tetrapropylammonium bromide (n-Bu4NBr) at 80°C under 15 bar of CO2 using SO/Br- and SO/complex molar ratios equal to 60 and 120, respectively. Only the Cr(III) complex was able to achieve good yields (>90%) of styrene carbonate in a reasonable time (7 h) [4,5]. Even better performances with Cr(III) could be achieved by replacing the t-butyl substituents in positions 3 and 5, by dimethylamino groups in position 4 of the ligand (N,N'-bis(4-dimethyaminosalicylidene)-1,2-phenylenediamine) (Fig.1) in principle due to the activation of CO2 via the formation of hydrogen carbonate in the vicinity of the Cr(III)-coordinated epoxide during the cycloaddition reaction.

The two best chromium (III) complexes were naturally tested within the context of the overall reaction for the conversion of styrene into styrene carbonate in the presence of O2 (3.5 bar) and CO2 (11 bar), that was carried out in a one-pot version at 80°C by combining the different components of the catalytic system in the following molar proportions: IBA/St/Bu4NBr/Cr complex: 250/120/2/1. Under these conditions, and contrary to what we had observed at 120°C [3], styrene carbonate was produced over a period of 23 h despite the presence of an excess of aldehyde. A yield of nearly 35% was obtained for the complex with the amino substituents, compared to 16% in the other case (Fig.2). Then, a heterogeneous version of this type of catalytic system will be presented. The quaternary ammonium salt and the Salophen-t-Bu Cr(III) complex were grafted onto mesoporous silica for recycling purpose and also to take advantage of complementary activation effects on the epoxide by residual silanols or aminopropyl groups used as linkers.

FIGURES



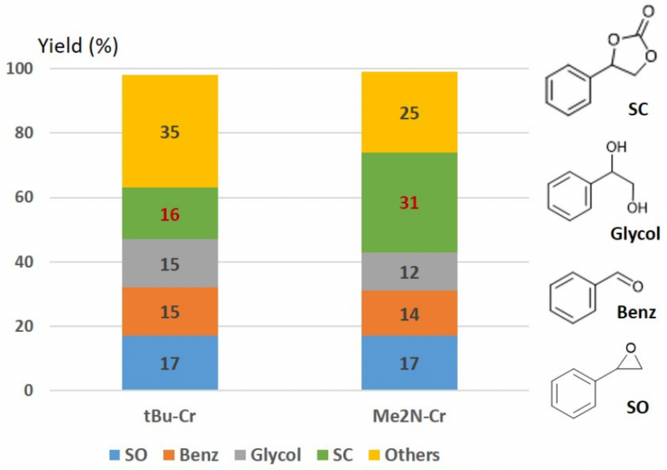


FIGURE 1

Series of Salophen chromium(III) complexes tested in the CO2 cycloaddition onto styrene oxide

FIGURE 2

Influence of the Salophen complex on the conversion of styrene and of the yields of products under O2 and CO2 atmosphere

(Cr complex/Bu4NBr/St/IBA : 1/2/120/250)

PhCN, 80°C, 3,5 bar O2, IBA, 11 bar CO2, 23 h

KEYWORDS

CO2 valorization | carbonates | epoxidation | tandem catalysis

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